80% of light of wavelength 520nm passed through a 0.25M solution contained in a cell of path length 1 cm. (4,4,4.5)

4. (a) Find the commutator of the operators $\frac{d}{dx}$ and $3x^2$.

(b) Arrange the bonds C – Cl, C – F and C – Br in order of increasing frequency of IR signal for stretching of the bond. Give reason for your answer.

(c) The quantum efficiency of a reaction is 0.55. A sample absorbs light of wavelength 260nm at the rate of 0.75 J min^{-1}. Calculate the moles of product formed in 30 minutes. (4,4,4.5)

[This question paper contains 8 printed pages.]

Your Roll No. ....

C

Sr. No. of Question Paper : 1573

Unique Paper Code : 42177925

Name of the Paper : DSE – Chemistry of d-block Elements, Quantum Chemistry and Spectroscopy

Name of the Course : **B.Sc. Program**

Semester : V

Duration : 3 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in total with **three** from **SECTION A** and **three** from **SECTION B**.
3. Attempt **SECTION A** and **SECTION B** on separate answer sheets.
4. Use of scientific calculator and Log table is allowed.

SECTION A

INORGANIC CHEMISTRY

Attempt **ANY THREE** questions. Attempt **any three** questions in this section. **All** questions carry equal marks.

1. (a) Name **any three** of the following complexes according to the IUPAC system of nomenclature:

   (i) $Na[Co(CO)_4]$

   (ii) $[Cr(H_2O)_4Cl(NCS)]NO_3$

   (iii) $[Co(NH_3)_6]\ [Cr(C_2O_4)_3]$

   (iv) $[(NH_3)_2Pt(Cl).(Cl)Pt(NH_3)_2]Cl_2$

   (b) Indicate the isomerism exhibited in the following pairs of compounds and give one method to distinguish between them :

   (i) $[Co(NH_3)_5Br]SO_4$ and $[Rh(NH_3)_5\ SO_4]\ Br$

   (ii) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ and $[Cr(H_2O)_6]Cl_3$

   (c) Give brief reasons for **any two** of the following :

2. (a) Find if the function $f(x) = ae^{x^2}$ is an Eigen function of the operator $\frac{d}{dx}$?

   (b) What is the significance of normalization condition?

   (c) What is phosphorescence? Draw jablonski diagram and explain the process of phosphorescence.

   (d) The absorption band in IR spectrum of $^{12}C^{16}O$ is at 2045 cm^{-1}. Calculate its zero point energy and force constant of the bond. (2,2,4,4.5)

3. (a) A particle of mass m is confined in a one dimensional box of length L. Calculate the probability of finding the particle between L/4 and L/2 if it is present in the ground state and is represented by the wave function $\psi = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}$.

   (b) As the number of conjugated atoms in a molecule increase the $\pi^* \rightarrow \pi$ transition shifts to higher wavelength. Explain.

   (c) Calculate the transmittance, absorbance and molar extinction coefficient of a solution which absorbs

(i) $[Mn(CN)_6]^{4-}$

(ii) $[Mn(Cl_4)]^{2-}$ (4.5,4,4)

SECTION B

Planck's constant, $h = 6.626 \times 10^{-34}$ Js;

Velocity of light, $c = 3 \times 10^8 ms^{-1}$

Mass of an electron, $m_e = 9.1 \times 10^{-31}$ kg

Attempt **any three** questions.

1. (a) Normalize the function $f(x)=\frac{x^2}{2}$ in the range $0 \le x \le a$.

(b) What is Lambert's law? How is it modified by Beer?

(c) The spacing of lines in the microwave spectrum of $^1H^{35}Cl$ is 11.2 cm^{-1}. Calculate the moment of inertia and bond length of the molecule. (4,4,4.5)

(i) Transition metals and their complexes have catalytic properties.

(ii) Ca & Sc^+ are isoelectronic but have different electronic configuration.

(iii) $CuSO_4.5H_2O$ is coloured and anhydrous $CuSO_4$ is colourless. (4.5,4,4)

2. (a) Write the formulae of **any three** of the following according to IUPAC convention :

(i) Potassium tetrahydroxidozincate(II)

(ii) μ-hydroxido-μ-superoxidobis{pentaammine-chromium(III)} chloride

(iii) Pentaamminesulphatorhodium(III) tetrahydroxidoferrate(II)

(iv) Potassium amminepentachloridoplatinate(IV)

(b) $[Co(NH_3)_5Cl]^{2+}$ undergoes ligand substitution reaction when treated with $NaNO_2$ to give two products A & B, depending on the experimental conditions. A & B are isometric pentaamine ions. Draw their structures and indicate the isomerism.

(c) Predict the appropriate choice and give brief reasons :

(i) Greater Value of Δ_0 $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$

(ii) Chelating ligand ethylenediamine, Pyridine

(4.5,4,4)

3. (a) The complex $[Cr(NH_3)_2 (C_2O_4)_2]$ exists in two isomeric forms A & B. A is optically active but B is not. Explain the reason briefly and draw the structures of A & B.

(b) Chromium(II) fluoride and Manganese(II) fluoride, both have a central metal ion surrounded by six Fluoride ligands. All the Mn-F bond lengths are equal, but two of the Cr-F bond lengths are shorter than the remaining four. Explain.

(c) Calculate CFSE in terms of Δ_0 of a d^3 metal ion placed in a tetrahedral field. Draw the splitting diagram. (4.5,4,4)

4. (a) For the complex ion $[Mn(H_2O)_6]^{3+}$, given mean pairing energy, P = 28,000 cm^{-1}, and magnitude of Δ_o is 21,000 cm^{-1}, calculate CFSE corresponding to high spin and low spin states. In which of the states the complex is more stable?

(b) The Latimer diagram for Fe in acidic medium is given below:

$$FeO_4^{2-} \xrightarrow{2.20} Fe^{3+} \xrightarrow{+0.77} Fe^{2+} \xrightarrow{-0.47} Fe$$

Answer the following questions :

(i) Is there any state which undergoes disproportionation? Explain.

(ii) Calculate skip step potential for Fe^{3+} ---- Fe change.

(iii) Is there any tendency of Fe^{2+} to reduce to Fe? Give reason for your answer.

OR

(b) Briefly discuss **any two** of the following :

(i) Limitations of Valence Bond Theory

(ii) Spectrochemical Series

(iii) Separation of lanthaniods by ion exchange method

(c) Using VBT predict the geometry and magnetic behaviour of :